PATENT ABSTRACTS OF JAPAN

(11)Publication number : **2001-307751**

(43)Date of publication of application : **02.11.2001**

(51)Int.Cl. H01M 8/02
C23C 14/14
C23C 14/24
C23C 14/34
H01M 4/90
H01M 8/10

(21)Application number : **2001-082609**

(22)Date of filing : **22.03.2001**

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(30)Priority

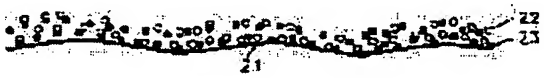
Priority number : **2000 200014551** Priority date : **22.03.2000** Priority country : **KR**
2000 200072128 **30.11.2000** **KR**

(54) MANUFACTURING METHOD FOR ELECTRODE-MEMBRANE ASSEMBLY AND FUEL CELL USING THE ASSEMBLY MANUFACTURING BY THE METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a manufacturing method for electrode-membrane assembly and a fuel cell using the assembly manufactured by this method.

SOLUTION: This manufacturing method includes a step of coating catalytic metal particles 23 on an ion-exchanged polymer membrane with a sputtering method, followed by a step of coating carbon particles 22 on this membrane with sputtering or arc discharge to form a catalyst layer 21 of nanoparticles, and succeeded by a step of bonding this membrane with the pole. Otherwise, this method includes a step of coating catalytic metal particles 23 and carbon particles 22 concurrently on a hydrogen ion-exchanged polymer membrane by the sputtering method to form a catalytic layer 21 of nanoparticles, followed by a step of bonding this membrane with the pole.



LEGAL STATUS

[Date of request for examination] 02.07.2001

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]	
[Date of final disposal for application]	
[Patent number]	3477644
[Date of registration]	03.10.2003
[Number of appeal against examiner's decision of rejection]	
[Date of requesting appeal against examiner's decision of rejection]	
[Date of extinction of right]	

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CLAIMS

[Claim(s)]
[Claim 1] The phase which coats the metal catalyst of a nano particle for the source of supply of a metal catalyst by sputtering on the hydrogen ion exchange poly membrane which has the switching function of a hydrogen ion, By carrying out sputtering of the carbonaceous source of supply on the hydrogen ion exchange poly membrane to which coating of said metal catalyst was carried out, or carrying out arc discharge The manufacture approach of the electrode-film assembly characterized by including the phase which performs coating processing of the carbon of a nano particle and forms a nano particle catalyst bed, and the phase of joining to an electrode the hydrogen ion exchange poly membrane in which said nano particle catalyst bed was formed.
[Claim 2] Whether the source of supply of said metal catalyst is platinum (Pt) independent, gold (Au), Palladium (Pd), a rhodium (Rh), iridium (Ir), a ruthenium (Ru), The alloy of the at least a kind of metal and platinum (Pt) which were chosen from the groups which consist of tin (Sn) and molybdenum (Mo), Or the manufacture approach of the electrode-film assembly according to claim 1 which is said both mixture and is characterized by the thing which was chosen from the groups which the source of supply of said carbon becomes from graphite and a carbon rod, and which is a kind at least.
[Claim 3] The manufacture approach of the electrode-film assembly according to claim 1 or 2 characterized by for the thickness of said catalyst bed being 10nm to 100nm, and the particle size of the metal catalyst by which coating was carried out, and carbon being 2nm to 10nm.
[Claim 4] The manufacture approach of an electrode-film assembly given in any 1 term of claims 1-3 to which the amount of catalyst loading per unit area of an electrode is characterized by being 0.2 mg/cm2 from 0.01 mg/cm2, and being 2 mg/cm2 from 0.1 mg/cm2 in DMFC (Direct Methanol Fuel Cell; direct methanol fuel cell) in PEMFC (Proton Exchange Membrane Fuel Cell; hydrogen ion exchange film fuel cell).
[Claim 5] The manufacture approach of an electrode-film assembly given in any 1 term of claims 1-4 to which the content of the metal catalyst by which coating was carried out on said hydrogen ion exchange poly membrane is characterized by being 25% to 85% to the mass of the sum total of the mass of a metal catalyst, and carbonaceous mass.
[Claim 6] It is the manufacture approach of an electrode-film assembly given in any 1 term of claims 1-5 characterized by for the pressure of gas being 10Pa to 1000Pa, and injection power being 100W to 400W in case sputtering of the source of supply of said metal catalyst or the carbonaceous source of supply is carried out.
[Claim 7] The manufacture approach of an electrode-film assembly given in any 1 term of claims 1-6 characterized by for the pressure of gas being 10Pa to 1000Pa, and a current value being below 100A in case [said] arc discharge is carried out.
[Claim 8] The manufacture approach of the electrode-film assembly characterized by to include the phase which performs coating processing with the metal catalyst of a nano particle, and the carbon of a nano particle, and forms a nano particle catalyst bed by carrying out sputtering of the source of supply of a metal catalyst, and the carbonaceous source of supply to coincidence on the hydrogen ion exchange

poly membrane which has the switching function of a hydrogen ion, and the phase join to an electrode the hydrogen ion exchange poly membrane in which said nano particle catalyst bed was formed.
[Claim 9] Whether the source of supply of said metal catalyst is platinum (Pt) independent, gold (Au), Palladium (Pd), a rhodium (Rh), iridium (Ir), a ruthenium (Ru), They are at least a kind of metal chosen from the groups which consist of tin (Sn) and molybdenum (Mo), an alloy with platinum (Pt), or said both mixture. The manufacture approach of the electrode-film assembly according to claim 8 characterized by the thing which was chosen from the groups which the source of supply of said carbon becomes from graphite and a carbon rod, and which is a kind at least.
[Claim 10] The manufacture approach of the electrode-film assembly according to claim 8 or 9 characterized by for the thickness of said catalyst bed being 10nm to 100nm, and the particle size of the metal catalyst by which coating was carried out, and carbon being 2nm to 10nm.
[Claim 11] The manufacture approach of an electrode-film assembly given in any 1 term of claims 8-10 to which the amount of catalyst loading per unit area of an electrode is characterized by being 0.2 mg/cm2 from 0.01 mg/cm2, and being 2 mg/cm2 from 0.1 mg/cm2 in DMFC in PEMFC.
[Claim 12] The mass of the metal catalyst by which coating was carried out on said hydrogen ion exchange poly membrane is the manufacture approach of an electrode-film assembly given in any 1 term of claims 8-11 characterized by being 25% to 85% to the mass of the sum total of the mass of a metal catalyst, and carbonaceous mass.
[Claim 13] The manufacture approach of an electrode-film assembly given in any 1 term of claims 8-12 characterized by for the pressure of gas being 10Pa to 1000Pa, and injection power being 100W to 400W in case sputtering of the source of supply of said metal catalyst or the carbonaceous source of supply is carried out.
[Claim 14] The manufacture approach of an electrode-film assembly given in any 1 term of claims 8-13 characterized by for the pressure of gas being 10Pa to 1000Pa, and a current value being below 100A in case [said] arc discharge is carried out.
[Claim 15] The fuel cell using the electrode-film assembly manufactured by the manufacture approach of an electrode-film assembly given in any 1 term of claim 1 to claim 14.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the manufacture approach of an electrode-film assembly of coming to join an electrode and a hydrogen ion exchange poly membrane, and the fuel cell using the electrode-film assembly manufactured by this manufacture approach.
[0002] This invention relates to the manufacture approach of the electrode-film assembly which comes to have the catalyst bed which has improved the magnitude of the carbon particle which is supporting the catalyst, and the fuel cell electric output characteristics come to improve by adopting the electrode-film assembly manufactured by this approach more at a detail.
[0003]
[Description of the Prior Art] The hydrogen ion exchange film fuel cell (Proton Exchange Membrane Fuel Cell:PEMFC) equipped with the poly membrane which has a hydrogen ion switching function is the clarification energy source of the future which may replace fossil energy, and has the description that power density and the transformation efficiency of energy are high. Moreover, while actuation in ordinary temperature is possible, since a miniaturization and sealing-izing are possible, it is possible to apply broadly in the field of pocket mold electronic equipment. In addition, the vocabulary and the "hydrogen ion exchange film" which are used below, and a "hydrogen ion exchange poly membrane" have the same semantics.
[0004] Said PEMFC is a power generative system which produces the electrical and electric equipment of a direct current from the electrochemical reaction of hydrogen and oxygen. The fundamental structure of such a cel is shown in drawing 1 . If drawing 1 is referred to, the fundamental structure of such a cel is the structure where the hydrogen ion exchange film 11 comes to intervene between the anodes and cathodes with which reactant gas is supplied.
[0005] Thickness consists of a solid-state polyelectrolyte which is 50-200 micrometers, and the hydrogen ion exchange film 11 shown in drawing 1 has the structure in which the anode was equipped with the catalyst bed 12 formed in the upper part with the anode supporters 14. Moreover, the cathode has the structure possessing the catalyst bed 13 formed in the upper part with the cathode supporters 15. Here, the anode supporters 14 and the cathode supporters 15 consist of a carbon cloth (carbon cross) or carbon paper (carbon paper). And surface treatment is performed so that water may tend to pass the hydrogen ion exchange film 11 and these anode supporters 14 and the cathode supporters 15 may become further, as supply of a reaction gas or a liquid becomes easy.
[0006] In drawing 1 , a reference number 16 shows the bipolar plate (amphipathy plate) which has the slot for insufflation, and this bipolar plate also has the function as a charge collector. While reactant gas is supplied, with an anode, oxidation reaction arises and, as for PEMFC which has structure which was described above, a hydrogen content child is converted into a hydrogen ion and an electron. At this time, a hydrogen ion is sent to a cathode through the hydrogen ion exchange film 11.
[0007] Moreover, while reactant gas is supplied, as for PEMFC which has structure which was described above, an oxygen molecule receives an electron by a reduction reaction arising in a cathode, it

is converted into oxygen ion, and this oxygen ion reacts with the hydrogen ion from an anode, and is converted into a water molecule.

[0008] On the other hand, although it has the same structure as PEMFC fundamentally described above, a direct methanol fuel cell (Direct Methanol FuelCell:DMFC) supplies the methanol of a liquid to an anode instead of hydrogen as a fuel for a reaction, according to an operation of a catalyst, oxidation reaction arises and a hydrogen ion, an electron, and a carbon dioxide generate it. Although such DMFC has low energy efficiency compared with PEMFC, since a fuel is supplied in the state of a liquid, there is an advantage of being easy to apply to pocket electronic equipment.

[0009] Drawing 2 is drawing showing typically the configuration of the catalyst bed with which the above mentioned fuel cell is equipped. As shown in drawing 2 , in the above mentioned fuel cell, the catalyst bed 21 is constituted including the metal particles 23 of the catalyst supported by the carbon particle 22, and the binder (binder) which is not illustrated. Here, said carbon particle 22 acts so that the reactant gas which flowed may be diffused and the reaction field of reactant gas may be extended, and in order that the metal particles 23 of a catalyst may advance oxidation reaction and reduction reaction of reaction fuel gas, i.e., hydrogen, a methanol, and oxygen, it plays an important role. At this time, even in case the bonding strength of a catalyst bed 21 and the hydrogen ion exchange film is made to hold appropriately and is continuously used for the binder (binder) which is not illustrated, it prevents that a catalyst bed 21 secedes from the hydrogen ion exchange film.

[0010] The metal particles of the catalyst which the above mentioned carbon powder comes to support are manufactured by the usual reduction. This reduction is the approach of returning the compound which holds the metal of a catalyst in the state of a cation, generating the metal of a catalyst, depositing only the metal of this catalyst on the front face of support like a carbon particle, and coating the metal of a catalyst on the surface of a carbon particle. It is as follows when how to manufacture a catalyst bed using the metal particles of the catalyst manufactured by such reduction is explained concretely.

[0011] First, after manufacturing Pt/C which comes to carry out coating of the metal-particles slack platinum (Pt) of the catalyst of an ultrafine particle with a magnitude of 2-5nm to the front face of a carbon particle (C) whose particle size is 0.1 micrometers, polytetrafluoroethylene is added as a binder (binder). Thus, after it deposits the obtained constituent in the shape of film and it is ****(ed) by the ionomer (polymer which has covalent bond between elements of macromolecule chain, and has ionic bond between macromolecule chains) solution, it dries and it is formed in a catalyst bed.

[0012] However, since the magnitude of a carbon particle becomes comparatively large with about hundreds times from dozens times by the approach of forming the aforementioned catalyst bed compared with the metal particles of a catalyst, it is difficult for the rate of the total surface area to this whole carbon particle product to become comparatively small, and for whenever [per unit volume of this carbon particle / catalytic activity] to become comparatively small as that result, and to form the catalyst bed which may demonstrate a catalysis comparatively greatly.

[0013] It is a big trouble to do only a comparatively small catalysis to the gas by which especially the catalyst bed formed by this approach since the touch area of the hydrogen ion exchange film and a catalyst bed became comparatively small by the approach of forming the aforementioned catalyst bed was generated by the hydrogen ion exchange film.

[0014] Moreover, in the fuel cell which has such a catalyst bed, since the uptake of the reaction in which the diffusion condition of reactant gas participates, or a current mainly occurs in the contact surface of the metal particles of a catalyst, and a carbon particle, the fuel cell which comes to have the conventional catalyst structure where many catalyst particles were supported by one carbon particle which has an above comparatively big particle size is not so efficient in respect of a catalysis or a generation-of-electrical-energy process.

[0015] In order to solve a trouble which was described above, the approach (U.S. Pat. No. 5,234,777) of forming a catalyst bed in the hydrogen ion exchange film directly through a decal process and the method (academic journal;Electrochemica Acta., Vol.42, No.10, pp.1587-1593) of making an electrode surface distribute the metal of a catalyst using the sputtering method are proposed.

[0016] By the approach of forming a catalyst bed in the hydrogen ion exchange film directly through

said decal process, the catalyst bed which cast the constituent for catalyst bed formation on another base material first, next was cast in this way, and was formed is exfoliated from a base material, and a catalyst film is obtained. Furthermore, a desired catalyst bed is completed by carrying out the laminating of this catalyst film on the hydrogen ion exchange film. However, the approach of forming a catalyst bed in the hydrogen ion exchange film directly through such a decal process is inherent in the following troubles.

[0017] That is, in the catalyst bed completed by the above approaches, since the effectiveness of making the touch area of a catalyst bed and the hydrogen ion exchange film increasing to some extent needs to form a catalyst film from the catalyst system with which the catalyst was supported by the carbon powder which has the magnitude of about several micrometers of a certain thing, it is difficult for it to make the front face of the hydrogen ion exchange film fully distribute a catalyst particle by constraint by the magnitude of this carbon particle. Such a phenomenon can be explained using drawing 2 and drawing 3 .

[0018] Drawing 2 is drawing showing typically the configuration of the catalyst bed with which the above mentioned fuel cell is equipped, and drawing 3 is a 500,000 time enlargement by the transmission electron microscope photograph (Transmission electron microscope:TEM) observation which shows the condition of the catalyst bed in a Prior art. As shown in drawing 2 , the catalyst bed 21 is formed of the carbon particle 22 with which, as for the conventional catalyst bed formed by the approach of forming a catalyst bed in the hydrogen ion exchange film directly through such a decal process, the metal particles 23 of a catalyst were supported, and, as for the distributed condition of such a catalyst particle in a catalyst bed 21, is greatly influenced of the magnitude of a carbon particle 22 by it. Moreover, as shown in drawing 3 , in the conventional catalyst bed formed by the approach of forming a catalyst bed in the hydrogen ion exchange film directly through such a decal process, degree of dispersion of such a catalyst particle is comparatively low.

[0019] Therefore, in order to obtain the electrode which has the power density of the electrical and electric equipment beyond a constant level, the amount of supply of reactant gas increases at the time of actuation of the fuel cell which was made to increase the amount of the catalyst used, and was equipped with ** and such a catalyst bed if it was ****. Since this leads to making the price increase, it is not desirable while increasing the weight and the volume of a fuel cell of a final product it not only reducing the use effectiveness of a catalyst, but. Moreover, there is demerit in which the forming cycle comparatively performed under an elevated temperature and high-pressure conditions is indispensable in order to join the hydrogen ion exchange film and a catalyst bed, and the hydrogen ion exchange film tends to deteriorate by such forming cycle.

[0020] moreover, by the approach of making an electrode surface distributing the metal of a catalyst using the aforementioned sputtering method While the metal particles of a catalyst trespass upon the interior of the hole of a porous electrode and the use effectiveness of a catalyst falls Since coating of the metal particles of such a catalyst is carried out on the carbon particle of the magnitude which is about several micrometers, it becomes difficult to join a catalyst bed to the front face of the hydrogen ion exchange film with which electrochemical reaction advances appropriately, and there is a trouble that the use effectiveness of a catalyst falls.

[0021]

[Problem(s) to be Solved by the Invention] The purpose of 1 of this invention is in view of a trouble which was described above to offer the manufacture approach of an electrode-film assembly that improve the property of the magnitude of the carbon particle which is supporting the catalyst, and use effectiveness of a catalyst and supply of a fuel are performed efficiently.

[0022] Moreover, other purposes of this invention are by adopting the electrode-film assembly manufactured by said approach to offer the fuel cell which raised electric output characteristics.

[0023]

[Means for Solving the Problem] This invention for attaining the purpose of 1 of said this invention The phase which coats the metal catalyst of a nano particle for the source of supply of a metal catalyst by sputtering on the hydrogen ion exchange poly membrane which has the switching function of a

hydrogen ion, By carrying out sputtering of the carbonaceous source of supply on the hydrogen ion exchange poly membrane to which coating of said metal catalyst was carried out, or carrying out arc discharge The manufacture approach of the electrode-film assembly characterized by including the phase which performs coating processing of the carbon of a nano particle and forms a nano particle catalyst bed, and the phase of joining to an electrode the hydrogen ion exchange poly membrane in which said nano particle catalyst bed was formed is offered. (Claim 1)

[0024] Moreover, the manufacture approach of the electrode-film assembly concerning this invention In claim 1, as a source of supply of said metal catalyst [whether it is platinum (Pt) independent and] Or gold (Au), palladium (Pd), a rhodium (Rh), iridium (Ir), The alloy of the at least a kind of metal and platinum (Pt) which were chosen from the groups which consist of a ruthenium (Ru), tin (Sn), and molybdenum (Mo), Or gold (Au), palladium (Pd), a rhodium (Rh), iridium (Ir), At least a kind of metal chosen from the groups which consist of a ruthenium (Ru), tin (Sn), and molybdenum (Mo), and mixture with platinum (Pt) are used. As a source of supply of said carbon It is characterized by the thing which was chosen from the groups which consist of graphite and a carbon rod and which use a kind at least. (Claim 2)

[0025] Furthermore, the manufacture approach of the electrode-film assembly concerning this invention is characterized by for the thickness of said catalyst bed being 10nm to 100nm, and the particle size of the metal catalyst by which coating was carried out, and carbon being 2nm to 10nm in claims 1 or 2. (Claim 3)

[0026] And the manufacture approach of the electrode-film assembly concerning this invention is characterized by for the amount of catalyst loading per unit area of an electrode being 0.2 mg/cm2 from 0.01 mg/cm2 in PEMFC (Proton Exchange Membrane Fuel Cell; hydrogen ion exchange film fuel cell), and being 2 mg/cm2 from 0.1 mg/cm2 in DMFC (Direct Methanol Fuel Cell; direct methanol fuel cell) in any 1 term of claims 1-3. (Claim 4)

[0027] Moreover, the manufacture approach of the electrode-film assembly concerning this invention is characterized by the content of the metal catalyst by which coating was carried out on said hydrogen ion exchange poly membrane being 25% to 85% to the mass of the sum total of the mass of a metal catalyst, and carbonaceous mass in any 1 term of claims 1-4. (Claim 5)

[0028] Furthermore, in case the manufacture approach of the electrode-film assembly concerning this invention carries out sputtering of the source of supply of said metal catalyst, or the carbonaceous source of supply in any 1 term of claims 1-5, the pressure of gas is 10Pa to 1000Pa, and it is characterized by injection power being 100W to 400W. (Claim 6)

[0029] And in any 1 term of claims 1-6, the pressure of gas is 10Pa to 1000Pa, and the manufacture approach of the electrode-film assembly concerning this invention is characterized by a current value being below 100A, in case [said] arc discharge is carried out. In addition, this current value has the magnitude which it is stabilized [magnitude] and produces said arc discharge at least. (Claim 7)

[0030] This invention for attaining the purpose of 1 of said this invention by carrying out sputtering of the source of supply of a metal catalyst, and the carbonaceous source of supply to coincidence again on the hydrogen ion exchange poly membrane which has the switching function of a hydrogen ion The manufacture approach of the electrode-film assembly characterized by including the phase which performs coating processing with the metal catalyst of a nano particle and the carbon of a nano particle, and forms a nano particle catalyst bed, and the phase of joining to an electrode the hydrogen ion exchange poly membrane in which said nano particle catalyst bed was formed is offered. (Claim 8)

[0031] Moreover, the manufacture approach of the electrode-film assembly concerning this invention In claim 8, as a source of supply of said metal catalyst [whether it is platinum (Pt) independent and] Or gold (Au), palladium (Pd), a rhodium (Rh), iridium (Ir), The alloy of the at least a kind of metal and platinum (Pt) which were chosen from the groups which consist of a ruthenium (Ru), tin (Sn), and molybdenum (Mo), Or gold (Au), palladium (Pd), a rhodium (Rh), iridium (Ir), at least a kind of metal chosen from the groups which consist of a ruthenium (Ru), tin (Sn), and molybdenum (Mo), and mixture with platinum (Pt) were used, and it was chosen as a source of supply of said carbon from the groups which consist of graphite and a carbon rod -- a kind is used at least. (Claim 9)

[0032] Furthermore, the manufacture approach of the electrode-film assembly concerning this invention is characterized by for the thickness of said catalyst bed being 10nm to 100nm, and the particle size of the metal catalyst by which coating was carried out, and carbon being 2nm to 10nm in claims 8 or 9. (Claim 10)
[0033] The manufacture approach of the electrode-film assembly concerning this invention is characterized by for the amount of catalyst loading per unit area of an electrode being 0.2 mg/cm2 from 0.01 mg/cm2 in PEMFC, and being 2 mg/cm2 from 0.1 mg/cm2 in DMFC in any 1 term of claims 8-10 further again. (Claim 11)
[0034] And mass of the metal catalyst by which coating of the manufacture approach of the electrode-film assembly concerning this invention was carried out on said hydrogen ion exchange poly membrane in any 1 term of claims 8-11 is characterized by being 25% to 85% to the mass of the sum total of the mass of a metal catalyst, and carbonaceous mass. (Claim 12)
[0035] Moreover, in any 1 term of claims 8-12, in case the manufacture approach of the electrode-film assembly concerning this invention carries out sputtering of the source of supply of said metal catalyst, or the carbonaceous source of supply, the pressure of gas is 10Pa to 1000Pa, and it is characterized by injection power being 100W to 400W. (Claim 13)
[0036] Moreover, in any 1 term of claims 8-11, the pressure of gas is 10Pa to 1000Pa, and the manufacture approach of the electrode-film assembly concerning this invention is characterized by a current value being below 100A, in case [said] arc discharge is carried out. In addition, this current value has the magnitude which it is stabilized [magnitude] and produces said arc discharge at least. (Claim 14)
[0037] This invention for attaining other purposes of said this invention offers the fuel cell using the electrode-film assembly manufactured by the manufacture approach of an electrode-film assembly given in any 1 term of claim 1 to claim 14. (Claim 15)
[0038]
[Embodiment of the Invention] Hereafter, the gestalt of desirable operation of this invention is explained to a detail with reference to the attached drawing. In addition, this invention can be suitably changed, as long as it is not limited only to the gestalt of this operation and is based on the technical thought of this invention. First, the "electrode-film assembly" of the vocabulary used by this invention is defined. An "electrode-film assembly" means the structure where the laminating of a catalyst bed and the electrode is carried out to these both sides one by one the core [a hydrogen ion exchange poly membrane].
[0039] If it is in the manufacture approach of the electrode-film assembly concerning this invention, the hydrogen ion exchange poly membrane which comes to provide a catalyst bed is manufactured by coating with the metal of a catalyst first the hydrogen ion exchange poly membrane which has the switching function of a hydrogen ion, and coating with carbon the front face on which coating of the metal of this catalyst was carried out after that, or carrying out coating processing of the metal and carbon of a catalyst at coincidence. At this time, the metal and carbon of a catalyst by which coating processing was carried out come to have the nano grain size which follows on changing the conditions of sputtering and arc discharge, and consists of various magnitude.
[0040] The catalyst bed concerning this invention has structure as shown in drawing 4 , drawing 5 , drawing 6 , and drawing 7 , respectively. Drawing 4 is a drawing in which the structure of the catalyst bed concerning this invention is shown typically here, and drawing 5 , drawing 6 , and drawing 7 are the photographs which expanded the structure of the catalyst bed which starts this invention, respectively by 500,000 times by transmission electron microscope (Transmission electron microscope:TEM) observation, and photoed it. If drawing 4 , drawing 5 , drawing 6 , and drawing 7 are referred to, it is possible for a catalyst bed to make the thin film which comes to carry out eburnation for the carbon particle which has the magnitude of nano meter order on a hydrogen ion exchange poly membrane, and a metal catalyst particle to be distributed over homogeneity and to not only be to constitute, but form. Therefore, if such a carbon particle and a metal catalyst particle use the catalyst bed which has the structure distributed over homogeneity, the activity of a catalyst can be raised compared with the conventional catalyst bed (see drawing 2 and drawing 3), and it will become possible to raise the use

effectiveness of this catalyst.
[0041] It is as follows when the manufacture approach of the catalyst bed in the electrode-film assembly concerning this invention is explained to a detail. First, in order to advance smoothly coating processing of the metal catalyst and carbon to a substrate slack hydrogen ion exchange poly membrane top, a hydrogen ion exchange poly membrane is pretreated. Since an efficient reaction is produced after coating of a metal catalyst and the carbon particle is carried out, such pretreatment is carried out.
[0042] The process of such pretreatment introduces the hydrogen ion exchange poly membrane which passed through the washing process in the reaction chamber by which coating processing with a metal catalyst and carbon is performed, and removes the moisture of the front face of a hydrogen ion exchange poly membrane under vacuum conditions. And as for the pretreatment process of the vacuum drying of the front face of the hydrogen ion exchange poly membrane which does in this way and removes the moisture of the front face of a hydrogen ion exchange poly membrane, and the coating process of the metal catalyst mention later and carbon, it is desirable to perform, after make the rim section of said hydrogen ion exchange poly membrane fix to the support frame which has predetermined magnitude so that the front face of a hydrogen ion exchange poly membrane may be hold evenly.
[0043] Subsequently, the metal catalyst of the shape of a particle which carries out sputtering of the source of supply of a metal catalyst to one field of the hydrogen ion exchange poly membrane pretreated by doing in this way, and has the magnitude of nano meter order in it is coated. Here, at least a kind of metal chosen from the groups which are platinum (Pt) independent or consist of gold (Au), palladium (Pd), a rhodium (Rh), iridium (Ir), a ruthenium (Ru), tin (Sn), and molybdenum (Mo) as a source of supply of said metal catalyst, an alloy with platinum (Pt), or said both mixture is used.
[0044] It is desirable to use the target of the bulk which consists of Pt as a source of supply of a metal catalyst in PEMFC (Proton Exchange Membrane Fuel Cell; hydrogen ion exchange film fuel cell), and to use especially, the target of the bulk which consists of a presentation containing Pt and Ru in DMFC (Direct Methanol Fuel Cell; direct methanol fuel cell) in respect of the use effectiveness of a catalyst. And as for especially the magnitude of the particle of said metal catalyst, it is desirable that it is 2-10nm. namely, the time of the magnitude of the particle of a metal catalyst having such range -- the activity of a catalyst -- more -- high diligent **** -- it becomes like.
[0045] All the conventional general sputtering approaches can apply the sputtering approach of said metal catalyst, and the magnetron DC (direct current) sputtering approach is desirably used for it. The process in which coating of said metal catalyst is carried out by this approach is as follows.
[0046] First, inert gas is introduced in the reaction chamber by which coating processing with a metal catalyst and carbon is performed, the plasma of this inert gas is generated, and the particle of the plasma state of inert gas is formed in this plasma.
[0047] Then, the particle of the plasma state of this inert gas is accelerated towards the target of bulk, and sputtering (balking) of the metal atom is carried out by movement of the particle of the plasma state of this accelerated inert gas from the target of bulk.
[0048] And the metal particles by which sputtering (balking) was carried out by doing in this way are conveyed on the front face of a hydrogen ion exchange poly membrane continuously [the metal particles which are formed in the flux (amounts, such as metal particles which cross the flat surface in per unit time amount, and flow) of the shape of more uniform plasma of a magnetron, and are contained in the flux of this plasma state], and coating of the metal of a catalyst is carried out to this front face. According to such a coating process, it is possible to make homogeneity distribute more the metal catalyst of the shape of a particle which has the magnitude of nano meter order.
[0049] The coating conditions of said sputtering can be suitably changed according to the particle size of the metal of the catalyst considered as a request, and the degree-of-dispersion property of the metal of a catalyst. For example, the inert gas as reactant gas is poured in, holding the degree of vacuum in a reaction chamber to 10 - 6 or less Pa. At this time, it is desirable to use the mixed gas which makes it come as inert gas to mix argon gas or argon gas, and gaseous helium.
[0050] At this time, argon gas is used in order to mainly carry out sputtering of the metal particles directly from the target of said bulk. Moreover, after sputtering of said metal particles is carried out from

the target of bulk and they are formed in the plasma state, the metal particles of this plasma state extinguish a part of kinetic energy gradually by colliding mutually or colliding with the particle of inert gas. It comes to realize by adding gaseous helium and adjusting that addition comparatively easily [adjusting appropriately the decrement of the kinetic energy which these metal particles have] in that case. It becomes possible as the result to adjust the porosity of a metal coating layer suitably. In addition, with the fuel cell for which the electrode-film assembly which comes to have the coating layer of such a metal catalyst was used, there is a trouble that transfer of fuel gas tends to become difficult, the ** case which the coating layer of this metal catalyst makes that porosity lower, is formed, and is formed by carrying out eburnation of the metal catalyst more of it.

[0051] In case such sputtering is performed, while the pressure of gas is suitably adjusted within the limits of 10-1000Pa, as for the injection power of the spatter gun with which a sputtering system is equipped, it is desirable to be suitably adjusted within the limits of 100-400W.

[0052] That is, as for the pressure of the gas at the time of performing said sputtering, it is desirable that it is higher than the range of the upper limit of the pressure of the gas set up for the usual thin film formation. Here, porosity of the above "the usual thin film formation" is more small, and compactness means forming a higher thin film. Generally the range of the pressure of the gas set up for such usual thin film formation is 0.1-0.01Pa. Since it comes to have thing structure with the precise catalyst bed by which coating was carried out on the occasion of sputtering when the pressure of the gas in the case of sputtering is set to less than 10Pa, it becomes difficult to distribute the fuel of the shape of a gas or a liquid. Moreover, there is a trouble that it becomes difficult to carry out sputtering which it became difficult to form the uniform plasma when 1000Pa of pressures of gas was made to exceed, therefore was stabilized.

[0053] moreover, when the injection power of the spatter gun with which said sputtering system is equipped is smaller than 100W When the injection power of the spatter gun which it becomes difficult to obtain the catalyst bed which has a too weak particle size of ******, and is equipped with the power of injection power in said sputtering system is larger than 400W There is a trouble that it becomes difficult it to become difficult to form the uniform plasma, and for sputtering of the target of said bulk to comes to be carried out to an ununiformity, therefore to form the coating film of a desired metal catalyst. Subsequently, the field of both hydrogen ion exchange poly membranes can be coated with the metal layer of the catalyst of the shape of a particle which has the magnitude of nano meter order by performing repeatedly the sputtering process performed by doing in this way to one [of a hydrogen ion exchange poly membrane] remaining fields.

[0054] In addition, the amount of loading of the metal of the catalyst by which coating is carried out by doing in this way can be made into a necessary amount by adjusting suitably the terms and conditions of sputtering, such as time amount of sputtering, and injection electric energy. Moreover, the particle size of the metal of the catalyst at the time of doing in this way and coating of the metal of a catalyst being carried out is determined by the pressure of reactant gas, and the injection electric energy of sputtering.

[0055] Moreover, although the temperature of the target of said bulk rises in the process in which sputtering advances and heat occurs within a reaction chamber at the process of the above sputtering Thus, in order to prevent that the generated heat conducts to a hydrogen ion exchange poly membrane comparatively lacking in thermal resistance as much as possible It is desirable that perform sputtering continuously, it divides into about several times suitably until the amount of loading of the metal of a desired catalyst is rather obtained rather than it obtains the amount of loading of the metal of a desired catalyst, and it is made to carry out sputtering.

[0056] Thus, after carrying out loading of the metal of a catalyst to the field of both hydrogen ion exchange poly membranes, coating processing of the carbon of the shape of a particle which carries out sputtering of the carbonaceous source of supply to one field of a hydrogen ion exchange poly membrane where coating of the metal of the catalyst of the shape of a particle which has the magnitude of nano meter order was carried out, or has the magnitude of nano meter order with a cathode arc electric discharge method is carried out. The thing which was chosen here from the groups which consist of graphite and a carbon rod as a carbonaceous source of supply and which use a kind at least is desirable.

[0057] At this time, the process which carries out sputtering of the carbonaceous source of supply can be carried out by the same approach as the conditions at the time of carrying out sputtering of the source of supply of the metal of said catalyst. Moreover, when coating carbon by the above mentioned arc discharge, the thickness of the coating film of the carbon considered as a request with the carbon powder which has the magnitude of nano meter order comes to be obtained by adjusting suitably the injection electric energy and time amount for arc discharge.
[0058] When carrying out arc discharge of the source of supply of said carbon, the carbon particle which has the magnitude of nano meter order can be coated by adjusting a current value suitably so that the pressure of gas may be made to 10-1000Pa, and a current value may be made into within the limits below 100A and it may be carried out by stabilizing arc discharge. Since distribution of the fuel of the shape of a gas or a liquid becomes difficult in the fuel cell using the electrode-film assembly equipped with such a catalyst bed since the catalyst bed by which coating was carried out came to have had too precise membrane structure when it is sputtering as the pressure of said gas is less than 10Pa, it is not desirable. Moreover, when the pressure of said gas exceeds 1000Pa, there is a trouble that it becomes difficult it to become difficult to form the uniform plasma, and for sputtering of the target (carbonaceous source of supply) of said bulk to comes to be carried out to an ununiformity, therefore to form the coating film of a desired catalyst bed. Moreover, when a current value exceeds 100A, the carbon particle of a catalyst bed becomes uneven and there is a trouble that it becomes difficult to obtain the carbon particle which has the magnitude of desired nano meter order.
[0059] Subsequently, the catalyst bed which consists of a particle which coats the carbon of the shape of a particle which repeats the process of coating performed by sputtering of the source of supply of said carbon or the arc discharge of the source of supply of said carbon to the field of another side of an ion-exchange poly membrane, and has the magnitude of nano meter order, and has the magnitude of nano meter order is formed. As for the magnitude of the particle of the carbon by which coating was carried out as mentioned above here, it is desirable that it is 2-5nm, and it is constituted so that it may have the metal of the catalyst more desirably described above, a similar configuration, and magnitude. Thus, if a catalyst bed is constituted, it is desirable on the rate side face which the activity of a catalyst increases and raises the use effectiveness of a catalyst.
[0060] As for the thickness of the catalyst bed formed by the above mentioned approach, it is desirable that it is 10-100nm. If the thickness of this catalyst bed exceeds 100nm, it will become difficult to form effectively the interface of a hydrogen ion exchange poly membrane and a catalyst bed in respect of catalytic activity. Moreover, in PEMFC (Proton Exchange Membrane Fuel Cell; hydrogen ion exchange film fuel cell), it is desirable that it is within the limits of 0.01 - 0.2 mg/cm2, and when it is DMFC (Direct Methanol Fuel Cell: direct methanol fuel cell), to it, it is desirable [the final amount of catalyst loading per unit area of an electrode] that it is within the limits of 0.1 - 2 mg/cm2. When it becomes difficult to perform catalytic reaction with it and the upper limit of said range is exceeded, there is a trouble that the activity of a catalyst falls and the use effectiveness of a catalyst falls. [smooth when the final amount of catalysts per unit area of an electrode is under the lower limit of the aforementioned range]
[0061] Moreover, as for the content of the metal catalyst by which coating was carried out by the above mentioned approach, it is desirable that it is within the limits of 25 - 85 mass % to the mass of the sum total of the mass of a metal catalyst and carbonaceous mass, and it is more desirable especially that it is within the limits of 25 - 80 mass %. When the content of a metal catalyst is under the lower limit of said range, the activity of a catalyst falls, the use effectiveness of a catalyst falls, and in exceeding the upper limit of said range, diffusion of the fuel of the shape of a gas or a liquid becomes difficult with the fuel cell using an electrode-film assembly equipped with this metal catalyst.
[0062] When applied to the electrode-film assembly which requires the metal of the catalyst of a system or a 3 yuan system of 2 yuan for this invention, it is possible to use various kinds of spatter guns in which apply the alloy target or mosaic target which has a desired catalyst presentation, or it comes to install 2-3 sorts of targets separately.
[0063] If it coats with particle-like the metal and carbon of a catalyst which have the magnitude of nano

meter order and a nano particle catalyst bed is formed as described above When the metal and carbon of a catalyst permeate even the interior of the cavity of the front face of a hydrogen ion exchange poly membrane Compared with the structure of the catalyst bed in the technique of the conventional electrode-film assembly typically shown in drawing 2 , each reaction effectiveness of the oxidation reaction produced on the front face of a hydrogen ion exchange poly membrane and a reduction reaction comes to increase. Moreover, it becomes possible to constitute the catalyst bed formed in both sides of a hydrogen ion exchange poly membrane from a thin film. Therefore, especially in DMFC which comes to adopt such a hydrogen ion exchange poly membrane, there is an advantage that a methanol can control the phenomenon in which it is crossed, by holding the catalyst bed by the side of an anode in the gestalt of a thin film.

[0064] While coating processing of the carbon may be first carried out after coating the upper part of a hydrogen ion exchange poly membrane with a metal catalyst as explained above, coating processing of a metal catalyst and the carbon may be carried out at coincidence. In this case, the sputtering approach is used as an approach of carrying out coating processing of a metal catalyst and the carbon at coincidence. It is desirable to use the magnetron sputtering approach, in carrying out sputtering especially of the metal catalyst, and to use the RF (Radio frequency:RF) sputtering method in the case of carbon.

[0065] Furthermore, it is as follows when the manufacture approach of the electrode-film assembly concerning this invention equipped with the catalyst bed concerning this invention constituted by doing in this way is explained. After locating an electrode in both sides of the hydrogen ion exchange poly membrane by which coating processing was carried out with the metal catalyst and carbon of the shape of a particle which has the magnitude of said nano meter order respectively, heat-treatment and pressure treatment are performed to this electrode, and the electrode-film assembly concerning this invention is completed by combining an electrode and a hydrogen ion exchange poly membrane. At this time, the temperature of said heat-treatment is temperature (125 degrees C when [Nafion :] it is Nafion) which a hydrogen ion exchange poly membrane softens, and the pressure of said pressure treatment is about 0.196Pa (200 kgf/cm2). At this time, the carbon cloth (carbon cross) or carbon paper (carbon paper) which has necessary electrical conductivity as said electrode can be used.

[0066] Then, said electrode-film assembly is respectively equipped with BAIPORA and a plate, and a fuel cell is completed. BAIPORA and a plate have a slot for fuel supply, and have the charge collector function here.

[0067]

[Example] It is made to contrast with the example which starts this invention in the fuel cell using the electrode-film assembly hereafter manufactured by the manufacture approach of the electrode-film assembly concerning this invention, and this approach, and the example of a comparison with which the requirement of this invention is not filled, and explains to a detail. In addition, this invention can be suitably changed, as long as it is not limited only to the following examples and based on the technical thought of this invention.

[0068] [Example 1] First, in the example 1 concerning this invention, Nafion 115 (Nafion115; Du Pont make) was used as a hydrogen ion exchange poly membrane, and this hydrogen ion exchange poly membrane was pretreated as follows. First, in order to do easy an activity within the vacuum chamber of said hydrogen ion exchange poly membrane, after producing the standing ways which consist of stainless steel and exposing the active region (25cm2) of magnitude predetermined by said hydrogen ion exchange poly membrane using these standing ways, the part of the angle of the outside of said hydrogen ion exchange poly membrane was made to fix to these standing ways. And the hydrogen ion exchange poly membrane fixed in this way was left for 10 minutes under the vacuum ambient atmosphere, and moisture was removed. This pretreatment was performed by holding a degree of vacuum to ten to 6 Pa.

[0069] Thus, the magnetron sputtering method was used for one field of the pretreated hydrogen ion exchange poly membrane, and it was coated with the metal catalyst of Pt. The conditions of this magnetron sputtering are as follows. That is, the mixture of gas of argon gas and gaseous helium was used as reactant gas.

[0070] And this mixture of gas used the blending ratio of coal of argon gas and gaseous helium as 1:1. Furthermore, while holding the pressure to 100Pa, sputtering was performed, having used as 300W injection power of the spatter gun with which a magnetron sputtering system is equipped. In addition, although total time amount of sputtering was made into 400 seconds, sputtering was performed in 2 steps by a unit of 200 second so that the temperature of the target comparatively heated too much by sputtering of long duration might not conduct to a hydrogen ion exchange poly membrane.
[0071] Subsequently, both sides of a hydrogen ion exchange poly membrane were coated with the metal catalyst of Pt after completing the process of the above mentioned sputtering by repeating and giving the process of such sputtering to the field of another side of an ion-exchange poly membrane. In addition, when the magnitude of the particle of Pt catalyst in which coating was carried out by the process of such sputtering was measured by transmission electron microscope (Transmission electron microscope:TEM) observation, it became clear that it is about 3nm.
[0072] Then, the hydrogen ion exchange poly membrane which is carried out in this way and by which coating of the metal catalyst of Pt was carried out to both sides was introduced into the arc chamber in the condition of having made it fixing to the standing ways made from stainless steel. Then, the predetermined electrical potential difference was impressed to the electrode with which it was equipped with the graphite bar made from graphite (graphite) to make it the discharge current of 40A flow, and one field of a hydrogen ion exchange poly membrane was coated with carbon. And both sides of a hydrogen ion exchange poly membrane were coated with carbon by repeating the coating process of such carbon to the field of another side of said hydrogen ion exchange poly membrane, and performing it. Thus, the hydrogen ion exchange poly membrane concerning this invention by which coating of the metal catalyst and carbon of Pt was carried out to both sides was obtained.
[0073] here -- the pressure in an arc chamber -- about 10Pa -- holding -- arc discharge time amount -- the business of one field of a hydrogen ion exchange poly membrane, and the field of another side it is alike, respectively, and receive, carry out by a unit of 10 seconds, and according to such arc discharge -- the process of carbon coating -- one field of a hydrogen ion exchange poly membrane, and the field of another side -- it was alike, respectively, and it received and carried out by a unit of 3 times repeatedly. The content of the metal catalyst of Pt contained in the catalyst bed in which coating was carried out by such process is 0.02 mg/cm2, and a carbonaceous content is 0.06 mg/cm2, and the magnitude of the carbon of metal catalyst **** of particle-like Pt became clear [that each is 3nm] by TEM observation. Here, the content of the metal catalyst which consists of Pt was what is equivalent to 25 mass % to the sum total of the mass of the metal catalyst of Pt, and carbon.
[0074] moreover, as supporters of the anode contained in the electrode joined to the hydrogen ion exchange poly membrane produced by doing in this way, or a cathode the carbon paper (carbon paper --) with which water proofing was performed by the tetrafluoroethylene-hexafluoropropylene copolymer with which 20:80 appears comparatively and it comes to blend tetrafluoroethylene and hexafluoropropylene The product made from E-Tek was used and the electrode-film assembly (membrane-electrode assembly:MEA) which performs bonding processing which combines these supporters with the hydrogen ion exchange poly membrane to which coating of said catalyst bed was carried out, and starts this invention was manufactured.
[0075] In addition, said bonding processing was carried out by making about 0.196Pa (200 kgf/cm2) load act, and pressurizing it for about 3 minutes at 125 degrees C, using a hotpress. Thus, PEMFC (Proton Exchange Membrane Fuel Cell; hydrogen ion exchange film fuel cell) which starts this invention using the completed electrode-film assembly was manufactured.
[0076] [Example 2] The metal catalyst bed of Pt-Ru which consists of a metal catalyst of Pt and a metal catalyst of Ru by the DC (direct current) sputtering method was formed in one field of a hydrogen ion exchange poly membrane (Nafion115; Du Pont make) where the anode was joined, and coating of the carbon was carried out to this and coincidence by the RF (high frequency) sputtering method.
[0077] Furthermore, like the field of another side of said hydrogen ion exchange poly membrane where the cathode was joined, coating of the metal catalyst and carbon of Pt was carried out to coincidence. Thus, the catalyst bed was formed in the front face of said hydrogen ion exchange poly membrane. It

was 100Pa, and the pressure of the conditions of DC sputtering to which the pressure of the reactant gas at this time totaled the partial pressure of argon gas and the partial pressure of gaseous helium is the same as that of said example 1, and carried out the conditions of RF sputtering by 300W.
[0078] By the same approach as an example 1, DMFC (Direct Methanol Fuel Cell; direct methanol fuel cell) using the electrode-film assembly MEA (membrane-electrode assembly) and this electrode-film assembly MEA as an example 2 concerning this invention was manufactured using the hydrogen ion exchange poly membrane which comes to provide the catalyst bed formed by such approach.
[0079] At this time, the content of the metal catalyst of Pt-Ru and the metal catalyst of Pt by which coating was carried out to the front face of a hydrogen ion exchange poly membrane was 1.5 mg/cm2 respectively, and the carbonaceous content was 0.375 mg/cm2. Thus, it became clear by TEM observation that the particle size of the metal catalyst constituted and carbon shows about 5-10nm distribution. The content of a metal catalyst was what corresponds to 80% to the mass of the sum total of the mass of a metal catalyst, and carbonaceous mass here.
[0080] [Example 1 of a comparison] After manufacturing the catalyst bed which contains this metal catalyst particle using the metal catalyst particle (20%Pt/C, product made from E-Tek) of Pt which deposited on the carbon base material by the reduction performed electrochemically by the spray approach, the electrode-film assembly MEA (membrane-electrode assembly) and PEMFC (Proton Exchange Membrane Fuel Cell; hydrogen ion exchange film fuel cell) were manufactured by the same approach as said example 1.
[0081] As for the metal catalyst of Pt used in this example 1 of a comparison, that content is 0.2 mg/cm2 and the content of this metal catalyst of Pt is [more / 10 times] from PEMFC of said example 1. And the carbonaceous content was 0.8 mg/cm2 and the content of the metal catalyst of Pt was what corresponds to 20% to the mass of the sum total of the mass of this metal catalyst of Pt, and carbonaceous mass. Thus, the particle size of the metal catalyst by which coating was carried out is about 5nm, and it became clear by TEM observation that a carbonaceous particle size is about 100nm.
[0082] [Example 2 of a comparison] If it removed that the content of Pt catalyst by which coating was carried out on the hydrogen ion exchange poly membrane was 0.02 mg/cm2, it carried out by the same approach as the example 1 of a comparison, and MEA (membrane-electrode assembly) and PEMFC (Proton Exchange Membrane Fuel Cell; hydrogen ion exchange film fuel cell) were manufactured.
[0083] [Example 3 of a comparison] After forming a catalyst bed with a spray method using the particle (60%Pt/C, product made from E-Tek) of the metal catalyst of Pt-Ru which consists of the metal catalyst of Pt and the metal catalyst of Ru which deposited on the base material which consists of carbon by the electrochemical reduction method, MEA (membrane-electrode assembly) and DMFC (Direct Methanol Fuel Cell; direct methanol fuel cell) were manufactured by the same approach as said example 2.
[0084] The content of the metal catalyst of said Pt-Ru used in this example 2 of a comparison is 8 mg/cm2 (Pt:Ru=1:1). Moreover, the content of the metal catalyst of Pt used in this example 2 of a comparison is 8 mg/cm2, and is [more / 5.3 times] from the catalyst bed of said example 2. And the content of the carbon by which coating was carried out in this example 2 of a comparison was 3.2 mg/cm2, and the content of the metal catalyst of Pt was what corresponds to 60% to the mass of the sum total of the mass of this metal catalyst of Pt, and carbonaceous mass. And the particle size of the metal catalyst of Pt by which coating was carried out by doing in this way is about 5nm, and it became clear by TEM observation that a carbonaceous particle size is about 100nm.
[0085] [Example 4 of a comparison] Except for the content of the metal catalyst of Pt-Ru which consists of the metal catalyst of Pt and the metal catalyst of Ru by which coating was carried out on the hydrogen ion exchange poly membrane, and the metal catalyst of Pt being 1.5 mg/cm2, MEA (membrane-electrode assembly) and DMFC (DirectMethanol Fuel Cell; direct methanol fuel cell) were manufactured by the same approach as the example 3 of a comparison.
[0086] After supplying the oxygen gas and hydrogen gas (the division ratio of hydrogen and oxygen; 1:1) which it comes to humidify and operating this PEMFC to PEMFC (Proton Exchange MembraneFuel Cell; hydrogen ion exchange film fuel cell) manufactured using respectively the electrode-film assembly of said example 1, the example 1 of a comparison, and the example 2 of a

comparison, it evaluated about the polarization property and power density property of these PEMFC(s). (Refer to drawing 8)

[0087] As a result of evaluating the polarization property and power density property of these PEMFC (s), it is ****** which consists of the metals and carbon of the catalyst for which the catalyst bed of said example 1 has the magnitude of the shape of a particle of nano meter order so that the TEM observation photograph shown in drawing 5 may also show. Consequently, the touch area of this catalyst bed and a hydrogen ion exchange poly membrane can extend by such catalyst bed. It became clear that the structure property of a catalyst bed is improving.

[0088] And if it is in PEMFC manufactured using the electrode-film assembly of said example 1 as shown in drawing 8 , it turns out that the output density property and a polarization property are improving compared with PEMFC manufactured using the electrode-film assembly of the example 1 of a comparison, and the example 2 of a comparison.

[0089] Next, after supplying 2M-methanol solution and air to DMFC (Direct Methanol Fuel Cell; direct methanol fuel cell) manufactured using respectively the electrode-film assembly of said example 2, the example 3 of a comparison, and the example 4 of a comparison and operating it, it evaluated about the polarization property and power density property of these DMFC(s) (refer to drawing 9).

[0090] As a result of evaluating the polarization property and power density property of these DMFC(s), the structure of the catalyst bed of an example 2 consists of the metals and carbon of a catalyst which have the magnitude of the shape of a particle of nano meter order so that the TEM observation photograph shown in drawing 6 and drawing 7 may also show. Consequently, by such catalyst bed, the touch area of this catalyst bed and a hydrogen ion exchange poly membrane could extend, and it became clear that the structure property of a catalyst bed is improving.

[0091] And if it is in DMFC manufactured using the electrode-film assembly of said example 2 as shown in drawing 9 , it turns out that the polarization property and the power density property are excellent compared with the case of the example 3 of a comparison, and the example 4 of a comparison. Especially DMFC manufactured using the electrode-film assembly of an example 2 has the advantage that the phenomenon in which the catalyst bed by the side of an anode is crossed in a methanol by being formed and consisting of gestalten of a thin film is controlled unlike DMFC manufactured using the electrode-film assembly of the example 3 of a comparison, and example of comparison 4 **.

[0092]

[Effect of the Invention] According to this invention constituted, the following effectiveness is done so as explained above. That is, the touch area of this catalyst bed and a hydrogen ion exchange poly membrane can extend by the catalyst bed which consists of the metals and carbon of the catalyst which has the magnitude of the shape of a particle of nano meter order in case a catalyst bed is formed. Consequently, it becomes possible to make the particle of the metal of a catalyst permeate effectively in the detailed cavity of a hydrogen ion exchange poly membrane. Therefore, while being able to offer the electrode-film assembly with which the reaction effectiveness of the oxidation reaction produced on the front face of a hydrogen ion exchange poly membrane and a reduction reaction increased remarkably, the fuel cell which can increase generating efficiency remarkably can be offered by applying this electrode-film assembly to a fuel cell.

[0093] Moreover, since direct coating processing of the metal and carbon of such a catalyst can be carried out at a hydrogen ion exchange poly membrane and a catalyst bed can be formed, the productive efficiency of the fuel cell using an electrode-film assembly and this electrode-film assembly can be raised.

[0094] Furthermore, the structure of the catalyst bed formed of such coating processing can be appropriately designed so that the catalytic activity which produces efficiently oxidation reaction and reduction reaction of hydrogen gas and oxygen gas may be raised. The optimal amount of catalysts for oxidation reaction and reduction reaction of hydrogen gas and oxygen gas to make it efficiently generated as the result, Or the electrode-film assembly which consists of optimal amounts of catalysts for producing efficiently oxidation reaction and reduction reaction of the hydrogen gas and oxygen gas which are considered as a request can be offered. As a result, the content of the catalyst for

manufacturing the electrode-film assembly which has necessary catalytic activity can be effectively stopped now. Moreover, the structure of the catalyst bed which can distribute efficiently the fuel gas of the shape of a gas or a liquid can be formed intentionally, supply of fuel reactant gas becomes smooth and the fuel cell whose use effectiveness of a catalyst improved can be offered.

[0095] And since the catalyst bed by the side of an anode is producible in a thin film-like gestalt, when it is DMFC (Direct Methanol Fuel Cell; direct methanol fuel cell), a methanol can control the phenomenon in which it is crossed.

[0096] As mentioned above, although said example 1 and the example 2 were explained as reference about this invention, it does not pass over these examples to an instantiation-thing, but if it is those who have the knowledge usual by the technical field belonging to this invention, you should be able to understand that it is possible to originate various kinds of various deformation and other various equal examples based on these examples. Therefore, the technical protection range of this invention must be decided by technical thought of a claim.

[Translation done.]